

THERMAL DIFFUSION IN MONATOMIC-POLYATOMIC GAS MIXTURES

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ABSTRACT. Thermal diffusion factors of the systems H_2 -Xe, CO_2 -Kr and CO_2 -Xe have been measured by the two-bulb method over the temperature range from 330°-600°K. The results have been interpreted in terms of the Chapman-Enskog theory as well as the recent theory taking into consideration the effect of inelastic collisions on thermal diffusion phenomena.

INTRODUCTION

Recent theoretical work shows the necessity of considering the effect of inelastic collisions on thermal diffusion factor in polyatomic gases. The Chapman-Enskog theory (Chapman *et al.*, 1952) takes into consideration only the spherical part of the intermolecular potential and can be applied to polyatomic gases for properties which are not significantly affected by inelastic collisions. Schirdewahn, Klemm and Waldmann (1961) suggested a semi-empirical method for obtaining the effects of rotational degrees of freedom on thermal diffusion which is only applicable to isotopes. Subsequently, a more generalised approach to the problem has been given by Monchick, Yun and Mason (1963) and Monchick, Munn and Mason (1966). These theoretical treatments have been found not to be quite successful in interpreting existing thermal diffusion data on polyatomic gases. Another major factor which is hindering a proper explanation of thermal diffusion factors in polyatomic gases is the scarcity of reliable experimental data. Consequently, it is essential to have precise measurements of thermal diffusion factors in polyatomic gas mixtures. As a starting point it is preferable to study binary systems having one component as polyatomic. With this end in view, we have measured the temperature dependence of thermal diffusion factor of the systems H_2 -Xe, CO_2 -Kr and CO_2 -Xe in the range from 330°K to 600°K by the two bulb method. The systems have the interesting feature that carbon dioxide in contrast to hydrogen is expected to show the effect of inelastic collisions on thermal diffusion quite prominently.

EXPERIMENTAL

The all-metal two-bulb apparatus together with the accessories for the measurement of thermal diffusion factor has been described in detail by Deb and Barua (1967). The monatomic gases were supplied by the British Oxygen

Co., Ltd., and hydrogen gas (purity 99.95%) by Indian Oxygen Co., Ltd.. Carbon dioxide was prepared by heating BaCO_3 with PbCl_2 and the purity of the gas was tested in a mass spectrometer (Associated Electrical Industries, MS3 model). The temperature was assigned according to the following formula, (Brown, 1940).

$$\bar{T} = \frac{T_H T_C}{T_H - T_C} \cdot \ln \frac{T_H}{T_C} \quad \dots (1)$$

where T_H and T_C are the temperatures of the upper and the lower bulb respectively.

The separation factor q can be calculated from the relation,

$$q = \frac{(x_1/x_2)_{Top}}{(x_1/x_2)_{Bottom}} \quad \dots (2)$$

where x_1 and x_2 are the compositions of the lighter and the heavier molecules respectively. Thermal diffusion factor α can be calculated from the relation,

$$\alpha = \frac{\ln q}{\ln T_H/T_C} \quad (3)$$

The experimental procedure has already been described in an earlier paper (Deb *et al.*, 1967). The analysis of the samples after steady state has been reached was done by a mass spectrometer. The results of our measurements are shown in table 1 and figs. 1-3.

COMPARISON WITH EARLIER DATA

Heymann and Kistemaker (1959) obtained the thermal diffusion factor for the system H_2 -Xe by the two bulb method with Xe in trace. Their experimental values were higher than the theoretical thermal diffusion factor by 5 to 10%. Since in our experiment, the composition of Xe is far from trace, no direct comparison with their data is possible. However, our experimental values are also higher than the predicted values.

Cozens and Grew (1964) obtained the thermal diffusion factor for the mixture CO_2 -Kr and CO_2 -Xe in the temperature range 150°K to 1000°K, using one of the components in trace concentration. However, for these mixtures also, the compositions of the components in our experiments do not correspond to those of Cozens and Grew and hence no direct comparison is possible. Our experimental values are higher than those calculated on the L-J (12:6) model. One of the possible explanations should be the fact that the first approximation to the theoretical thermal diffusion factor may be considerably lower than the exact value. As had been pointed out by Mason (1957), error in the first approximation of thermal diffusion factor is much greater than for the other transport coefficients. The

general formulae given for higher approximations are very complicated and have been calculated by Mason (1957) and Saxena *et al.*, (1958) only for mixtures containing one component in trace.

INTERPRETATION OF THE DATA

The thermal diffusion factor α can be represented on the Chapman-Cowling first approximation as (Hirschfelder, *et al.*, 1964),

$$\alpha = A(6C_{12}^* - 5) \quad (4)$$

where C_{12}^* is a ratio of collision integrals and A is a function of masses, molefractions and potential parameters. For polyatomic gas mixtures the convergence of α is not known satisfactorily. Consequently, we shall confine our calculation of α to the first approximation. For the calculation of α the Lennard-Jones (12:6) potential has been used. The force constants taken were those determined from experimental viscosity data and the unlike interactions were approximated by the usual combination rules. The calculated values of α thus obtained from eq. (4) are shown in figs. 1-3 together with the experimental values of α .

TABLE I

Experimental values of thermal diffusion factors

H ₂ -Xe(H ₂ = 18.0%)		CO ₂ -Kr(CO ₂ = 37.5%)		CO ₂ -Xe(CO ₂ = 47.0%)	
T	α	T	α	T	α
337	0.31	350	0.17	383	0.23
397	0.34	390	0.18	421	0.24
468	0.36	438	0.19	469	0.27
534	0.38	471	0.20	520	0.30
		529	0.21	566	0.33
		572	0.21	601	0.36
		611	0.21		

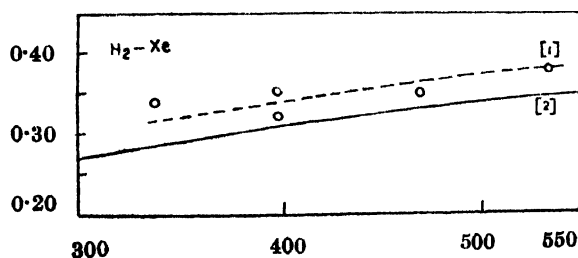


Fig. 1. Experimental and theoretical curves for the thermal diffusion factor α of the system H₂-Xe.

- [1] Experimental
- [2] Lennard-Jones (12 : 6)
- 0 Experimental points

As discussed earlier eq. (4) does not include the effect of inelastic collisions. In order to take this factor into account Monchick, Munn and Mason (1966) have recently given a treatment by solving the generalised Maxwell-Stefan equation. This theory has been found not to be quite successful in interpreting the existing thermal diffusion factor data for polyatomic gas mixtures (Monchick *et al.*, 1966 and Ghosh *et al.*, 1967). Consequently, we have tested this theory only for the CO₂-Xe system for which deviation from the Chapman-Enskog theory is maximum. According to this method the thermal diffusion factor can be written to the first approximation as,

$$\alpha_{ij} = \frac{1}{5k} \frac{\mu_{ij}(6C_{ij}^* - 5)}{n[D_{ij}]_1} \cdot \left(\frac{\lambda_j}{x_j M_j} - \frac{\lambda_i}{x_i M_i} \right) \quad (5)$$

where μ_{ij} is the reduced mass of the system. D_{ij} the diffusion coefficient, λ 's represent the thermal conductivities and x 's the mole fractions. By making some approximations λ can be expressed as (Monchick *et al.*, 1966),

$$\lambda_i \approx 4x_i \sum_{\alpha=1}^N \Lambda_{i\alpha} \left\{ x_\alpha + \sum_{\beta=1}^N \left[(\Delta\alpha_{\alpha\beta}^{10,10}) \left(\sum_{\gamma=1}^N \Lambda_{\beta\gamma} x_\gamma \right) - \left(\frac{x_\beta}{\mathcal{L}_{\beta\beta}^{01,01}} \right) (\Delta\mathcal{L}_{\alpha\beta}^{10,01}) \right] \right\} \dots (6)$$

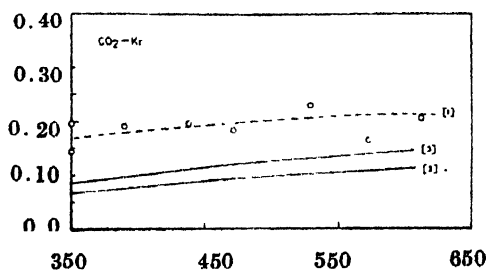


Fig. 2. Experimental and theoretical curves for the thermal diffusion factor α of the system CO₂-Kr.

[1] Experimental

[2] Lennard-Jones (12:6)

[3] Lennard-Jones (12:6) using experimental thermal conductivity values of CO₂

0 Experimental points

where

$$\Lambda_{\alpha\beta} = \left| \frac{q\mathcal{L}_{q'}^{10,10}}{\delta_{\beta q'}} \right| \frac{\delta_{q\alpha}}{0} \left| \mathcal{L}_{q\alpha}^{10,10} \right|^{-1} \dots (7)$$

The expressions for $\mathcal{L}_{qq'}^{rs,t's'}$ and $\Delta\mathcal{L}_{qq'}^{rs,t's'}$ have been given in detail by Monchick *et al.*, (1965). The terms $\mathcal{L}_{qq'}^{rs,t's'}$ involve cross-relaxation times. The molecular parameters required for the calculation of λ were chosen in the manner

similar to that described by Monchick *et al.* (1966). The result thus obtained is shown in fig. 3.

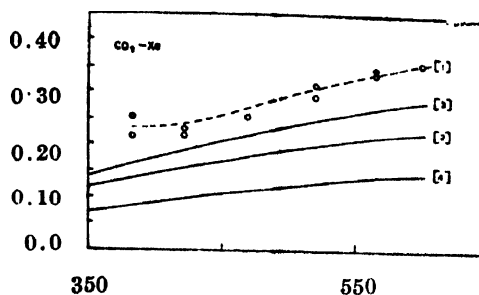


Fig. 3. Experimental and theoretical curves for the thermal diffusion factor α of the system $\text{CO}_2\text{-Xe}$.

- [1] Experimental
- [2] Lennard-Jones (12:6)
- [3] Lennard-Jones (12:6) using experimental thermal conductivity values of CO_2 .
- [4] Theoretical values calculated according to the formula of Monchick, (1966)
- 0 Experimental points

It may be seen that the consideration of the inelastic effects by the method of Monchick *et al.*, (1966) makes the agreement between theory and experiment worse than that obtained by using Chapman-Enskog theory. At present it is difficult to ascribe definitely the reason for this apparently anomalous result. It may, however, be due to the basic limitation of the Maxwell-Stefan equation or due to the number of approximations made in the evaluation of α from eq. (5).

It is also possible to express α on the Chapman-Enskog theory in terms of thermal conductivity. Thermal diffusion is dependent on the thermal conductivity of the components, which is also affected significantly by inelastic collisions. Therefore a tentative way of taking into accounts effects of inelastic collisions (at least partially) on thermal diffusion is to use experimental thermal conductivities in eq. (1) to calculate α . The results thus obtained for $\text{CO}_2\text{-Kr}$ and $\text{CO}_2\text{-Xe}$ systems by using experimental thermal conductivity data for CO_2 are shown in figs. 2 and 3. It may be seen that the agreement thus obtained is better than that obtained by all other methods.

The results obtained above show the inadequacy of our present knowledge of thermal diffusion phenomena in polyatomic gas mixtures. A more sophisticated theory to take into account effects of inelastic collisions on thermal diffusion is necessary.

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